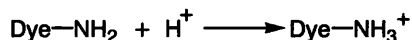


CHAPTER 18

Cationic dyes

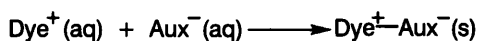
18.1 INTRODUCTION

Many of the initial synthetic dyes, such as Mauveine, had free basic amino groups capable of reacting with acids (Scheme 18.1). They were therefore originally named basic dyes. Molecules of these dyes are invariably organic cations and they are preferably called cationic dyes. They usually have brilliant colours and high tinctorial strength; some are even fluorescent. Many basic dyes are now obsolete because of their very poor light fastness on natural fibres but a few are still used for dyeing paper and leather and for making inks.



Scheme 18.1

Cationic dyes will dye fibres with anionic sites by a process of ion exchange (Scheme 1.2). This is usually a simple direct dyeing process. Anionic auxiliary products must be avoided as they may precipitate cationic dyes in the form of an organic salt (Scheme 18.2). In dyeing protein fibres with cationic dyes, acids retard dye absorption by suppressing the dissociation of the anionic carboxylate groups in the fibres (Scheme 7.1), thus making the fibre more cationic and inhibiting adsorption of dye cations. Cationic dyes have very low substantivity for cotton unless excessive oxidation has generated anionic carboxylate groups. For dyeing cotton with cationic dyes, the cotton was usually mordanted with tannic acid fixed with tartar emetic. The insoluble, anionic tannin attracts coloured dye cations (Section 1.1.2), just as it repels dye anions when on a nylon surface after back-tanning (Section 13.9.7).



Scheme 18.2

Today, the major use of cationic dyes is in dyeing anionic acrylic and modacrylic fibres and, to a much lesser extent, modified nylons and polyesters. Dye adsorption by acrylic fibres involves interaction between anionic sulphonate and sulphate polymer end groups and the cationic dye molecules (Scheme 4.5). In some acrylic fibres, anionic carboxylate groups are also involved (Section 18.4.1). Disperse dyes do not build up well on acrylic fibres and are only useful for pale shades. Dyeings of natural fibres with cationic dyes invariably have poor fastness to light. In direct contrast to this, acrylic fibres dyed with cationic dyes exhibit fairly good light fastness, and good fastness to washing. The improved resistance to fading is because of the limited access of water and oxygen into the more hydrophobic acrylic fibres. Access of both water and oxygen enhance the rate of colour fading on exposure to light (Section 24.3.4). Good washing fastness of acrylic materials dyed with cationic dyes is usual since most washing procedures are at temperatures well below the glass transition temperature of the fibrous polymer and the dye is therefore less likely to diffuse out of the fibre.

18.2 CHEMICAL STRUCTURES OF CATIONIC DYES

Cationic dyes belong to a variety of different chemical classes. Many of the older basic dyes were di- and triphenylmethane, heterocyclic azine, oxazine or polymethine, or aminoazo compounds (Figure 18.1). In many cases, the cationic charge is extensively delocalised over the entire dye molecule. Typical anionic counter ions include chloride, oxalate ($\text{C}_2\text{O}_4^{2-}$) and tetrachlorozincate (ZnCl_4^{2-}) ions. Since the introduction of acrylic fibres in the 1940s, new cationic dyes have been developed specifically for dyeing these fibres. Many of these have quaternary ammonium groups with a localised cationic charge that is not part of the chromophore (Figure 18.1).

18.3 PREPARATION FOR DYEING ACRYLIC FIBRES

18.3.1 Preparing the material

Poor preparation of the goods is usually the major cause of poor quality dyeings and preparation should be of the highest quality consistent with the final price of the material. The preparation of acrylic fibre materials may involve desizing of woven materials, scouring and bleaching. Combined desizing and scouring are often possible since relatively soluble sizing materials such as modified starch or

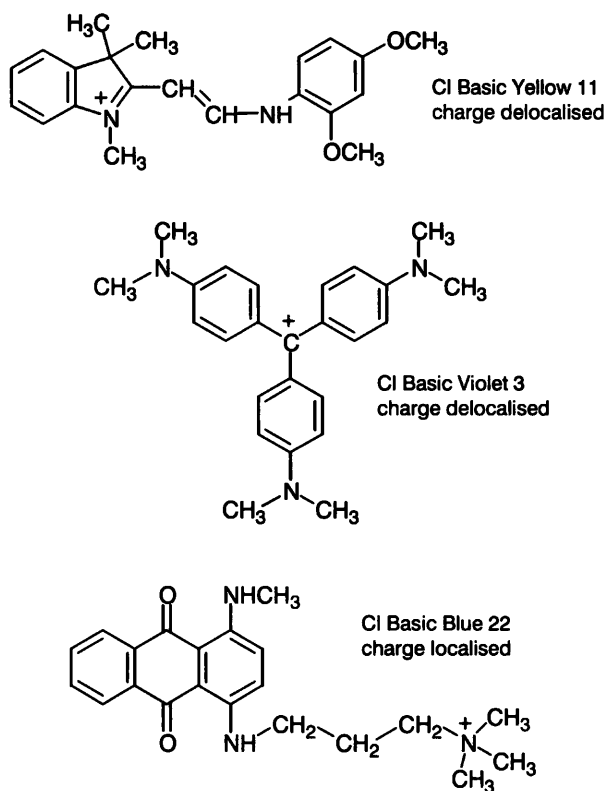
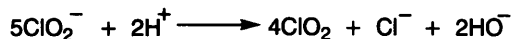


Figure 18.1 Chemical structures of some typical cationic dyes

polyvinyl alcohol are normally used. Scouring with weakly alkaline solutions of ammonia or trisodium pyrophosphate ($\text{Na}_3\text{HP}_2\text{O}_7$) is common. A non-ionic detergent is essential. Cationic auxiliary products may have substantivity for the anionic groups in the fibres and block dyeing sites whereas residues of anionic products will interact with and even precipitate the cationic dyes in the bath.

Acrylic materials sometimes have a slight yellow cast, usually a sign that drying was too severe. Bleaching is possible with sodium chlorite (NaClO_2) and formic acid or brightening with a fluorescent whitening agent. Some fluorescent whitening agents can be used in the presence of sodium chlorite, allowing combination of the two methods. Stabilisers that control chlorine dioxide emission (Scheme 18.3), such as borax or polyphosphates, should be used. A corrosion inhibitor such as sodium nitrate is essential when using steel equipment. Some cationic dyes are very sensitive to traces of chlorine and will rapidly fade giving poor colour yields, particularly when dyeing pale shades. An anti-chlor treatment

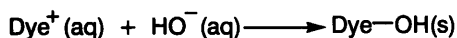
of fabric bleached with sodium chlorite may be necessary and small additions of sodium bisulphite or thiosulphate to the dyebath will avoid problems with cationic dyes sensitive to traces of chlorine in municipal water.



Scheme 18.3

18.3.2 Dyebath preparation

The dye powder is usually pasted with acetic acid and then mixed with boiling water. Cationic dyes with delocalised cationic charges are intensely coloured and it is essential to avoid dust escaping from the powders. Concentrated liquid dyes avoid this problem. Solid forms of these dyes are often not easy to dissolve because of their tendency to form gummy material. Preparation of a paste with methanol and addition of warm or hot water is sometimes a useful alternative. Some cationic dyes are not stable in boiling water. Many react with alkali to give colourless products such as the free amine from neutralisation of an ammonium ion group (reverse of Scheme 18.1), or a carbinol by reaction of the cationic group with hydroxide ion (Scheme 18.4). Dyeing with cationic dyes therefore invariably takes place in weakly acidic solution to avoid these problems.



Scheme 18.4

18.4 DYEING ACRYLIC FIBRES WITH CATIONIC DYES

18.4.1 Dyeing procedure

Acrylic fibres may contain a variety of different anionic groups. These include a limited number of terminal sulphate and sulphonate groups arising from the persulphate polymerisation initiator (Figure 3.2). In other types, there may be appreciable numbers of carboxylate groups from acrylic acid or similar comonomers added to the acrylonitrile before polymerisation (Section 4.4.1). These anionic groups are responsible for the substantivity of cationic dyes for such fibres. Figure 18.2 compares equilibrium dye adsorption as a function of pH for two types of acrylic fibres (A and B). Dyeing acrylic fibres with cationic dyes is carried

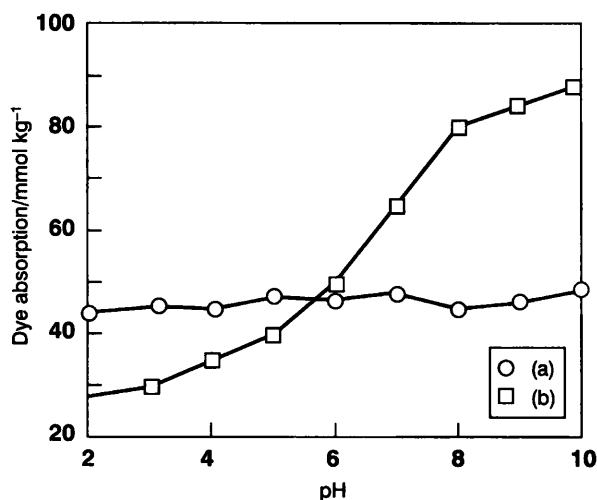


Figure 18.2 Equilibrium dye adsorption by acrylic fibres with only sulphate and sulphonate end-groups (a) and with carboxylate groups (b)

out in weakly acidic solution containing acetic acid and sodium acetate and a non-ionic wetting agent and dispersant. A small amount of sequestrant ensures that heavy metals do not interfere with chemicals in the solution.

The dye solution is often prepared by pasting with acetic acid, and a stable pH of 4.5 to 5.5 can be obtained by addition of sodium acetate to buffer the solution. Dyeing at around pH 5 suppresses the dissociation of any carboxylic acid groups in the fibre and thus controls the dyeing rate. Note the increased dye uptake of the acrylic fibre with carboxylic acid groups ((b) in Figure 18.2) as the acid groups dissociate and become anionic above pH 6. The number of carboxylate groups in an acrylic fibre varies from one type to the next. Level dyeing requires strict control of the pH and dyeing temperature, as well as the use of cationic retarding agents. The latter initially block the anionic sites in the fibre and are gradually replaced by the more substantive dye cations. An addition of up to 2.5 g l⁻¹ of anhydrous sodium sulphate helps to offset the negative surface charge and sodium ions weakly block anionic sites in the fibre. Both effects decrease the initial rate of dye absorption. Sodium sulphate is not as effective as cationic retarding agents that have some substantivity for the fibre.

Figure 18.3 shows a typical dyeing procedure. If dye additions are needed to give the correct shade, the bath temperature is first slowly reduced to below 80 °C. Acrylic materials are quite thermoplastic. They easily form crack marks and creases and texturised acrylic filaments also readily lose their characteristic

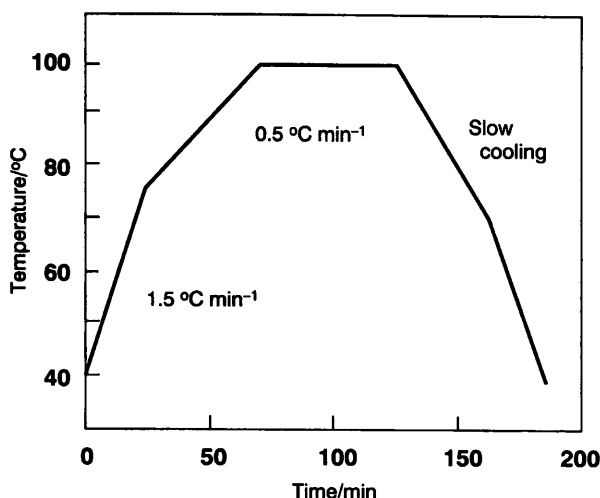


Figure 18.3 A typical procedure for dyeing acrylic material

bulk. After dyeing is complete, the bath is slowly cooled to 50–60 °C to avoid these problems. Rapid cooling by addition of cold water to the dyebath can be disastrous as it causes immediate setting of creases in the goods. The material is finally rinsed, and possibly given a mild scour with a non-ionic detergent and a little acetic acid plus a softening agent.

18.4.2 Problems in dyeing acrylic fibres with cationic dyes

Cationic dyes rapidly adsorb on all available surfaces of the acrylic fibres because of the polymer's negative surface potential in water. Once the fibre surfaces are saturated, the rate of isothermal dyeing is independent of the bath concentration and of the liquor ratio since the rate of diffusion of dye into the fibre is slow. Addition of sodium sulphate to the dyebath suppresses the rapid strike as sodium ions counteract the negative charge on the fibre surface.

Above the dyeing transition temperature (T_D) under the actual dyeing conditions, cationic dyes tend to exhaust very rapidly over a small range in temperature. Great care is needed at temperatures just above T_D to avoid unlevel dyeing. The rate of diffusion of the cationic dyes into the acrylic fibre is very slow below T_D because of the absence of the required polymer chain mobility. The rate of dyeing increases rapidly above T_D , and can double for every 2.5–3.0 °C increase in temperature. The corresponding increases in temperature needed to

double the dyeing rates of nylon and polyester are typically 10 and 5 °C, respectively, but at higher temperatures for polyester. Once the acrylic fibre becomes accessible, very careful temperature control is required. For this reason, once the bath temperature reaches 70–75 °C, the rate of heating is usually significantly decreased (Figure 18.3).

The careful temperature control required when dyeing acrylic fibres with cationic dyes is necessary to avoid unlevel dyeings. These dyes on acrylic materials have at best poor migration ability. Some newer types of more hydrophilic cationic dyes have low molecular weights and lower substantivity. They migrate more readily but attempted levelling by extended heating, or heating to a higher dyeing temperature, is dangerous because of the thermoplasticity of the fibre.

If the acrylic fibre has a significant number of carboxylate groups present, the dyeing pH will greatly influence the dyeing rate. The rate of exhaustion will increase with increase in the pH as more carboxylic acid groups dissociate. Thus, it is important to know the characteristics of the particular acrylic polymer in advance.

18.4.3 Dyeing mechanism

Although a simple ion exchange mechanism explains many effects in the dyeing of acrylic fibres, the process is probably more complex than this. Over-dyeing is not usually a problem as the fibres rarely accept more dye than corresponds to the number of anionic sites. The sulphonate and sulphate groups do not change with variation of the dyebath pH but this is not true for carboxylate groups. In acidic solution, carboxylate groups are protonated and their negative charge neutralised. For dyeings carried out at constant pH, the Langmuir isotherm provides a good description of the dyeing equilibrium (Section 11.1.1). The number of anionic sites in an acrylic fibre ($C_{\max}$) can be determined from the intercept of the graph of $1/C_f$ versus $1/C_s$ for a series of dyeings at equilibrium:

$$\frac{1}{C_f} = \frac{1}{C_{\max}} + \left(\frac{1}{KC_{\max}} \right) \times \frac{1}{C_s} \quad (1)$$

18.4.4 Dyeing retarders

The presence of either cationic or anionic auxiliary products in the dyebath controls the rapid strike and high rate of dyeing of cationic dyes on acrylic fibres. Cationic

retarders are organic ammonium salts with hydrophobic chains. Their adsorption on the fibre surface reduces the negative surface potential. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. They have moderate substantivity for acrylic fibres and may even be adsorbed before the dye is added to the bath to decrease the strike. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye. Boiling in the presence of some cationic retarder may give some degree of levelling although this invariably increases the risk of damaging the thermoplastic material. Other types of retarder are cationic polymers that adsorb on the surface of the fibres, decrease the negative surface potential and prevent easy passage of the dye into the fibre.

Anionic retarders complex with the cationic dye in the bath (Scheme 18.2) and decrease the number of free dye molecules in solution. Such anion-cation complexes easily precipitate and an anionic agent may have a non-ionic component to keep the complex in dispersion. They are less widely used than cationic retarders. Boiling a dyeing in a blank bath containing an anionic retarder will remove some dye. For complete stripping, bleaching with hypochlorite in the presence of acetic acid at around pH 6 is possible.

18.4.5 Compatibility of cationic dyes

Dyeing on shade with mixtures of dyes is most successful when the dyes used are compatible with one another. Ideally, the colour of the dyeing builds up gradually as the dyes are adsorbed, but always with the same hue. The complex behaviour of cationic dyes in mixtures complicates the determination of their dyeing compatibility. The rate of dyeing of any given dye, under given conditions, often changes significantly when other dyes are present. The rate is also dependent on the type and amount of retarding agent present in the dyebath. The dyer must rely on the dye supplier for information on the behaviour of the dyes and must often conduct his own dyeing trials. Because many variables influence the determination of cationic dye compatibilities, different dye suppliers use different methods of evaluation.

The key parameters determining the compatibility of dyes are the fibre saturation value and the combination constant or compatibility value. Knowledge of these parameters facilitates the selection of compatible dyes. The fibre saturation value determines the amounts of cationic dye or cationic retarder that will saturate all the fibre's anionic sites. The combination constant or compatibility value is based on the rate of dyeing.

One standard test (AATCC Test Method 141 [1]) evaluates a dye's combination constant or compatibility value k , a number from 1 (rapid dyeing) to 5 (slow dyeing). Dyeings of a given cationic dye are carried out in mixtures with each dye of a standard series of five blue or five yellow dyes. The series selected will have a yellow or blue hue markedly contrasting with the test dye. Thus, a violet cationic dye would be tested in mixtures with the series of yellow dyes rather than the blue series. The five dyes in each standard series have compatibility ratings from 1 to 5. At pre-selected times during the dyeing trials with mixtures of the test and standard dyes, a piece of the dyed material is replaced by undyed material and dyeing continued. For each mixture of test dye and standard dye, the colours of the successively dyed samples are examined. The combination constant ($k = 1$ to 5) for the test dye is that of the standard dye for which the series of dyeings are on shade. Compatible dyes should therefore have about the same k values. This type of information is available from the dye manufacturers.

Fibre saturation values give the number of anionic sites in the fibre (mmol kg^{-1}). This value ranges from about 25 up to 115 mmol kg^{-1} . The fibre saturation value determines the % owf of cationic dye or retarder that will saturate all the anionic sites. These amounts can be calculated if the molecular weight, total cationic charge and purity of the dye or retarder are known. Consider a cationic dye powder containing 50% pure dye with a single positive charge and a molecular weight of 400 g mol^{-1} . For an acrylic fibre with 25 mmol kg^{-1} of singly charged anionic sites, 2.0% owf of dye in the dyebath will saturate all the anionic sites if the dyebath exhaustion is 100%:

$$\text{Mass of dye} = 25 \frac{\text{mmol}}{\text{kg}} \times 400 \frac{\text{mg}}{\text{mmol}} \times \frac{100}{50} = 20\,000 \frac{\text{mg}}{\text{kg}} = 2.0\% \text{ owf} \quad (2)$$

Knowing how much dye will saturate the available sites in the fibre avoids excess dye adsorbed on the fibre surface, which leads to poor washing and rubbing fastness. When the total amount of dye is close to that required for fibre saturation, rapidly adsorbed dyes with low k values can block out slow dyeing dyes with high k values. For dyeing deep shades, the amount of cationic retarding agent is usually calculated so that its total charge plus that of the dye is that required to balance the charge of the fibre's anionic sites. Use of more than this quantity of retarder is wasteful and may reduce the exhaustion. The effect of cationic retarders is greater for dyes of higher k value. One of the difficulties in assessing cationic

dye compatibility values is that the values are different in the presence of cationic and anionic retarders.

18.5 DYEING MODIFIED POLYESTERS AND NYLONS

Polyester modified to have anionic sites by incorporation of 5-sulphophthalic acid (Figure 4.3) has a more open polymer structure and dyes more readily with disperse dyes. Because of the anionic groups, it can also be dyed with cationic dyes. This modified polymer is also more easily hydrolysed and more sensitive to heat setting before dyeing. Heat setting is carried out at a maximum temperature of 180 °C. Dyeing is usually under pressure in weakly acidic solution at temperatures not exceeding 120 °C.

Cationic dyes diffuse quite slowly into modified polyester fibres, even with added carrier. As in dyeing with disperse dyes, the carrier serves to open up the internal molecular structure of the polymer to allow more rapid dye diffusion into the fibres. Any carrier residue must be completely removed after dyeing to avoid reduced light fastness. When dyeing two-colour effects on blends of cationic-dyeable and regular polyester, with a mixture of cationic and disperse dyes, sufficient non-ionic emulsifier must be present to prevent precipitation of the cationic dye by anionic dye dispersing and carrier emulsifying agents.

Cationic-dyeable nylon fibres are also produced by incorporation of 5-sulphophthalic acid during polymerisation. They are used mainly for tone-in-tone and multi-colour effects in batch dyeing carpets from blends of regular and modified nylons. Dyeing is carried out at the boil in weakly acidic solution. A non-ionic emulsifying agent prevents the cationic dyes from precipitating in the presence of the anionic acid dyes used for the regular nylon.

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